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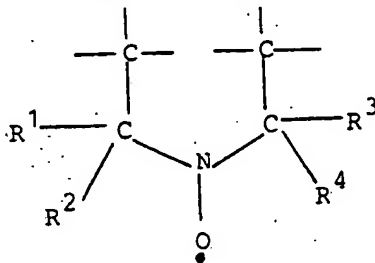
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(54) Photopolymerisable material

(57) A photopolymerisable material comprising a light-sensitive layer that contains compounds with N-oxyl structural units corresponding to the formula I



in which R¹-R⁴ may be the same or different and each represents H or alkyl, which are present in the layer, as polymer chain segments or substituents of a polymer, free and/or fixed by way of Coulomb reciprocal

The photopolymerisable material can be used for recording information, as a reproduction material, for the manufacture of printed circuits and relief images for printing plates, or for the manufacture of image-wise cured coatings.

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Photopolymerisable material

The invention relates to photopolymerisable materials suitable for recording information, especially in the form of reproduction materials for the production of printed circuits and relief images
5 for printing plates or for the manufacture of image-wise cured coatings.

It is known that many ethylenically unsaturated compounds may be polymerised using a photoinitiator
10 that forms radicals under the influence of light, these radicals initiating polymerisation. A number of compounds are known that form radicals under the influence of light according to a wide variety of mechanisms, the radicals then triggering
15 photopolymerisation (cf. H. Baumann, H.J. Timpe, H. Bottcher, Z. Chem. 23 (1983) 197).

Using these photoinitiators it is possible to build up photopolymerisable layers that in addition to the photoinitiator contain polymerisable or cross-
20 linkable compounds and a binder.

Since polymeric binders, and also other hydrocarbons, are oxidatively decomposed by atmospheric oxygen during storage and, further, because for many vinyl monomers and olefins the total activation energy
25 of the overall polymerisation without the initiation step is only 20 kJ mol^{-1} (J. Ulbricht, Grundlage der

Synthese von Polymeren, Akademie-Verlag, Berlin, 1978), advantageously inhibitors are added to the photopolymerisable layers. These inhibitors increase the storage stability of the photopolymerisable layers and thus prevent thermal fogging.

In the Patent Literature, inter alia the following classes of substance are described as inhibitors: phenols, for example p-methoxyphenol, t-butylcatechol, 1-naphthol, hydroquinone, quinones, for example p-benzoquinone, 2,5-diphenyl-p-benzoquinone; organic nitrogen compounds, for example amines (US-PS 4 167 415, 4 057 431, GB-PS 1 553 823, DE-OS 2 517 034, US-PS 4 053 317), N-nitroso compounds (DE-AS 1 291 620, US-PS 4 055 317, 3 615 629), thiourea, thiosemi- carbazides, thiosemicarbazones (DE-OS 3 013 170); organic phosphorus compounds, for example phosphines (US-PS 3 932 188, 4 097 283), phosphites (DE-OS 1 934 637, 2 104 958, DE-AS 1 098 712, US-PS 4 116 788); epoxides, for example 1,2-epoxydecane, glycidyl acrylate, styrene oxide (US-PS 4 146 453) and sulphur-organic compounds (US-PS 4-168 981, DE-OS 1 282 447). The inhibitors are generally used in a concentration of from 0.001 to 10 %, based on the compound to be polymerised.

In addition to the initiators, inhibitors, monomers and binders the photopolymerisable layers may optionally contain one or more additives, such as

plasticisers, pigments or dyes. Furthermore, oxygen quenchers, for example bis-tetrahydrofurancarboxylic acid amide (DE-AS 2 245 549) are also added to the photopolymerisable layers in order to suppress the
5 inhibiting influence of oxygen.

The photopolymerisable layer is applied to the support by applying a solution or dispersion of the individual components. There are suitable as supports a wide variety of natural or synthetic materials that
10 may be manufactured in the form of flexible or rigid sheets or plates.

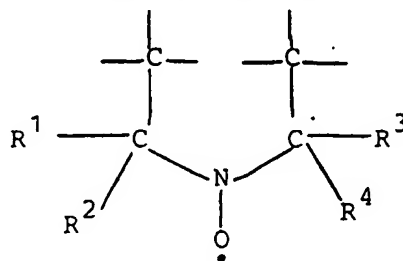
To produce the image the photopolymerisable layers are cured image-wise on exposure to light. The image-wise curing generally results not in visible images but
15 in an image-wise modification of the physical properties of the exposed areas owing to polymerisation or cross-linking. These changes in property can then be used in a subsequent developing step to produce an image (cf. H. Böttcher, J. Signal AM, 8 (1980) 405).
20 After development, relief images on the support material are obtained that can be used as printing formes or that after colouring produce transparencies or prints.

The aim of the invention is to develop photopolymerisable materials with improved reproduction of
25 detail and improved thermal stability in storage.

The problem underlying the invention is to find

organic compounds for photopolymerisable materials that suppress the reflected corona and stray light effects and prevent thermal fogging without adversely affecting the sensitivity (reactivity) of the material.

5 The present invention provides a light-sensitive composition comprising a material that contains N-oxyl structural units having the formula I



in which R¹ to R⁴ may be the same or different and
10 each represents H or alkyl.

The N-oxyl structural units may be free and/or in the form of polymer chain segments or substituents of a polymer that are fixed by means of Coulombic interactions and/or fixed by covalent bonding to the
15 rest to the polymer.

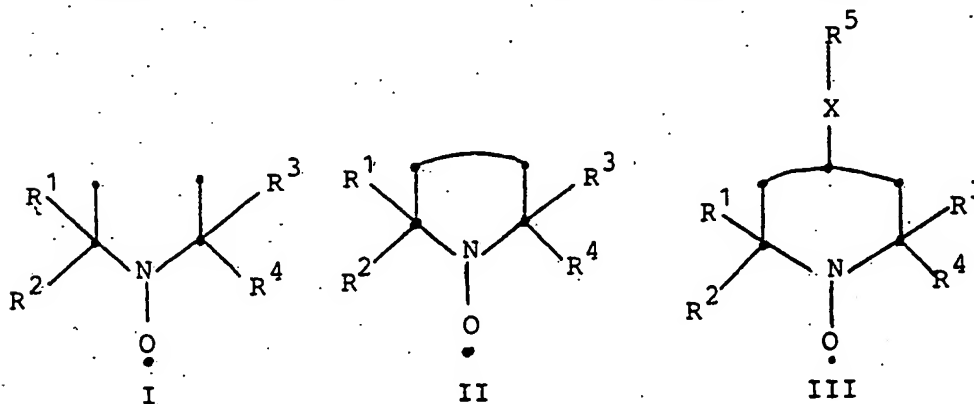
The present invention further provides a polymerisable material comprising a support and a light-sensitive layer according to the invention, together with optionally, one or more other layers, and
20 a method for the manufacture thereof.

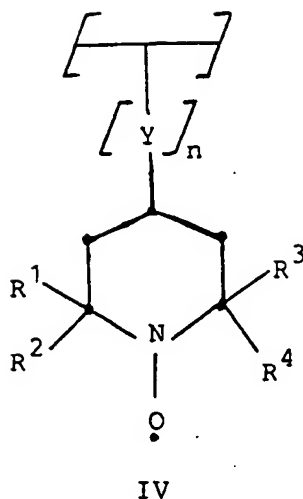
Furthermore the invention provides an image-bearing material, especially a printed circuit or printing plate, that has been manufactured by image-wise exposure of a polymerisable material according to

the invention followed by development.

Preferably compounds containing N-oxyl units that are added to the photopolymerisable layers contain cyclic N-oxyl units and especially sterically hindered cyclic 5- or 6-membered N-oxyls of the formula II in which R¹-R⁴ represent C₁-C₄ alkyl.

Advantageously, N-oxyls of the formula III are used and are present in the layer free and/or fixed by way of Coulomb interactions. Alternatively, or additionally, there may be used 6-membered ring N-oxyls of the formula IV that constitute from 1-50 mole % of a copolymer which is itself the layer binder or is added to the binder. The copolymer may be a copolymer that is derived from two, three or more monomer units.





R^1-R^4 may be the same or different and each represents
H or alkyl;

R^5 represents H, alkyl, aryl or a C_1-C_{18} acid
5 radical

R^6 represents H or CH_3

Y represents $\overset{O}{\parallel}C-$, alkylene or $-NR^6$,

n represents 0 or 1.

There are preferably used as substituents, for
10 R^1-R^4 : CH_3 ; for X : NR^6- , $-O-$; for R^5 : a C_1-C_{18} acid
radical, for example acetyl, benzoyl, salicyl, 2-ethyl-
hexanoyl; for R^6 : H, CH_3 ; for Y : a carboxy group
of a modified maleic acid unit, which together with one
or more other monomeric components, for example
15 styrene, methylmethacrylate, modified maleic acid
units, vinyl acetate, vinyl ether, α -methyl styrene,
propylene and other α -olefins, forms a copolymer.

It is also possible, however, to use polymeric N-oxyis that contain in addition to polymer-bonded N-oxyi substituents polymer-bonded piperidine radicals.

The photopolymerisable layers furthermore contain
5 organic compounds that have one or more polymerisable groups (monomers). The concentration of N-oxyis in the layer is from 10 to 10^4 ppm, based on monomer, depending on the monomer used. Furthermore, the photopolymerisable layers preferably contain a natural
10 or synthetic binder. The binder additive is especially advantageous if the compounds to be polymerised that are used are liquid substances. Suitable as binders are polymers or polymer mixtures that after exposure to light exhibit adequate solubility with respect to the
15 developer. Suitable polymers are, inter alia, gelatin, polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of maleic acid anhydride with styrene, o-methylstyrene, propylene, methyl methacrylate. The resistance to diffusion of the N-oxyis used is
20 increased by the use of binders having carboxyl groups.

To initiate the photopolymerisation there are added to the photopolymerisable layers initiators that form radicals under the influence of light according to
25 a wide variety of mechanisms, the radicals then triggering polymerisation or cross-linking. Plasticisers, pigments or dyes may also be added to the

photopolymerisable layers, depending on the intended use.

The photopolymerisable layers are best prepared by applying a solution or dispersion of all the individual components to the support. Suitable as a support are a wide variety of natural or synthetic materials, which may be manufactured in the form of flexible or rigid sheets or plates, such as, for example, copper, oriented polyester film, laminated papers, glass, aluminium with a coating of aluminium oxide, silicon and wood.

To produce the image the photopolymerisable materials are cross-linked by exposure to light, that is to say are image-wise cured. The exposure to light of the layers produced in accordance with the invention is effected using, for example, high pressure mercury lamps, ultra-high pressure xenon lamps or halogen lamps, or other lamps customarily used in reproduction technology. Sunlight, too, is suitable for the exposure. After image-wise exposure, development is carried out with a solvent or solvent mixture suitable for all components of the system. The time required for development depends on the layer thickness, the binder used and the temperature. The developing time is, however, generally < 10 minutes.

The following examples illustrate the invention.

Example 1

A mixture consisting of 60 parts of styrenemaleic acid butyl semiester copolymer, 50 parts of penta-erythritol tetraacrylate, 2 parts of Michler's ketone, 10 parts of benzophenone, 10 parts of diphenyliodonium chloride, 0.02 parts of N-oxyl of the formula III in which R^1-R^4 represent CH_3 , R^5 represents CH_3-CO- and X represents $-NH-$, 200 parts of butanol and 620 parts of methanol is cast using a 0.25 mm doctor blade on PETP (polyethylene terephthalate) film and dried at room temperature.

Mask exposure is carried out for 10 seconds using a high pressure mercury lamp, HBO 500, at a distance of 80 cm. After development with 2 % strength aqueous Na_2CO_3 solution a relief image is obtained which can be coloured, for example, with Solamin light Turkish blue.

Example 2

A mixture consisting of 77 parts of styrenemaleic acid butyl semiester copolymer, 43 parts of N,N-dimethylaminopropylacrylamide, 2 parts of Michler's ketone, 10 parts of benzophenone, 10 parts of diphenyliodonium chloride, 0.015 part of the N-oxyl of the formula III in which R^1-R^4 represents CH_3 , R^5 represents CH_3CO- and X represents $-NH-$, 600 parts of methanol and 250 parts of butanol is applied

using a 0.1 mm doctor blade to an aluminium plate with a coating of aluminium oxide.

The dry layer thickness after drying at room temperature is 8 μ m.

5 Image-wise exposure of the material is carried out for 15 seconds with an HBO 500 at a distance of 80 cm. After development with water a relief image is obtained which can be coloured, for example, with Walk brilliant red.

10 Example 3

A mixture consisting of 60 parts of styrenemaleic acid propyl semiester copolymer, 40 parts of penta-erythritol tetraacrylate, 10 parts of methylene bisacrylamide, 2 parts of Michler's ketone, 10 parts of
15 benzophenone, 10 parts of diphenyliodonium chloride, 0.02 parts of the N-oxyl of the formula III in which R^1 - R^4 represent CH_3 , R^5 represents $PhCO$ and X represents $-O-$, 600 parts of methanol and 250 parts of propanol is applied to cellite film (cellulose
20 triacetate film) using a 0.25 mm doctor blade and dried at room temperature. Image-wise exposure is carried out for 10 seconds with an HBO 500 at a distance of 80 cm.

After development with a 1 % strength KOH solution a relief image is obtained which can be coloured, for
25 example, with Wofalan black.

Example 4

A mixture consisting of 76 parts of a styrenemaleic acid butyl semiester copolymer, 40 parts of N,N-dimethylaminopropyl acrylamide, 10 parts of triethanol-
5 amine trisacrylate, 2 parts of Michler's ketone, 10 parts of benzophenone, 10 parts of diphenyliodonium chloride, 1 part of a polymeric N-oxyl of the formula IV which is composed of 50 mole % of styrene, 48 mole % of maleic acid butyl semiester and 2 mole % of maleic
10 acid 4-(2,2,6,6-tetramethylpiperidino-N-oxyl)semiamide, 250 parts of butanol and 600 parts of methanol, is cast using a 0.25 mm doctor blade directly onto PETP sheet and then dried at room temperature.

The image-wise exposure is carried out for 10
15 seconds with an HBO 500 at a distance of 80 cm. After development with water a relief image is obtained which can be coloured, for example, with Solamin light Turkish blue.

Example 5

20 A mixture consisting of 50 parts of gelatin, 25 parts of polyvinyl alcohol, 2 parts of m,m'-disulphonated Michler's ketone, 10 parts of the sodium salt of p,p'-benzophenonedisulphonic acid, 10 parts of diphenyliodonium hydrogen sulphate, 40 parts of
25 acrylamide, 40 parts of N,N-dimethylaminopropyl acrylamide, 20 parts of methylene bisacrylamide, 0.04 part

of the N-oxyl of the formula III in which R^1 - R^4
represent CH_3 , R^5 represents CH_3CO and X
represents $-\text{NH}-$, 1200 parts of water and 300 parts of
methanol is applied using a 0.1 mm doctor blade to an
5 aluminium plate coated with aluminium oxide, and dried
at room temperature.

Image-wise exposure is carried out for 15
seconds using an HBO 500 at a distance of 80 cm. After
development with water it is possible to recognise a
10 relief image which can be coloured, for example with
methylene blue.

Example 6

A mixture consisting of 50 parts of polyvinyl-
pyrrolidone, 10 parts of 2-methylstyrenemaleic acid
15 butyl semiester, 30 parts of pentaerythritol tetra-
acrylate, 10 parts of trisacryl formal, 10 parts of
glyceryl triacrylate, 2 parts of Michler's ketone, 10
parts of benzophenoneone, 10 parts of diphenyliodonium
chloride, 0.01 part of the N-oxyl of the formula III in
20 which R^1 - R^4 represent CH_3 , R^5 represents
 $\text{CH}_3\text{CO}-$ and X represents $-\text{O}-$, 250 parts of ethanol and
600 parts of methanol is cast using a 0.25 mm doctor
blade and then dried at room temperature.

Image-wise exposure is carried out for 10 seconds
25 using an HBO 500 at a distance of 80 cm. Development
is carried out with methanol and produces a relief

image which can be coloured, for example, with methylene blue.

Example 7-12

The unexposed material specimens of Examples 1 to 5 6, after having been dried at room temperature, are stored at 50°C for 2.5 hours. The specimens treated in this manner are exposed, developed and coloured using analogous procedures to those of Examples 1 to 6. Completely fog-free relief images are obtained, and 10 the reproduction of detail corresponds to that of the materials of Examples 1 to 6.

Examples 13-18

To test the thermal stability in storage, in each case 100 µl of the mixtures of Examples 1 to 6 are each 15 applied to nickel platelets of a size of 1 cm² and then dried. With these specimens the reactivity of each material is determined photocalorimetrically and scaled in relation to 1. Further specimen platelets with mixtures from Examples 1 to 6 are stored at 50°C 20 for 2.5 hours after having been dried, and are then examined photocalorimetrically. Table 1 shows once again the very good thermal stability in storage of the materials examined.

Examples 19-24 (comparison Examples without N-oxyl)

Mixtures from Examples 1 to 6, but without the addition of the respective N-oxyls, are applied to the respective supports analogously to Examples 1 to 6, dried and then stored for 2.5 hours at 50°C. The materials treated in this manner are exposed and developed in accordance with Examples 1 to 6. Completely fogged relief images, without reproduction of detail are obtained, which are not suitable for recording information.

10 Examples 25-30 (comparison Examples without N-oxyl)

100 μ l in each case of the mixtures of Examples 19 to 24 are each applied to nickel platelets of a size of 1 cm², dried, stored for 2.5 hours at 50°C and then examined photocalorimetrically. After the heat treatment the reactivity of the specimens has dropped by 90 % (cf. Table 1).

Table 1: Relative reactivity of the photopolymerisable mixtures before and after storage for two and a half hours at 50°C

5	Example	Layer composition according to Example	Relative reactivity
	13	1	0.98
	25	1 (without N-oxyl)	0.12
	14	2	1
10	26	2 (without N-oxyl)	0.10
	15	3	0.98
	27	3 (without N-oxyl)	0.12
	16	4	1
	28	4 (without N-oxyl)	0.13
15	17	5	0.94
	29	5 (without N-oxyl)	0.06
	18	6	0.99
	30	6 (without N-oxyl)	0.11

20 Example 31 (State of the Art)

A mixture consisting of 60 parts of styrenemaleic acid butyl ester copolymer, 50 parts of pentaerythritol tetraacrylate, 2 parts of Michler's ketone, 10 parts of benzophenone, 10 parts of diphenyliodonium chloride,
 25 0.2 part of hydroquinone monomethyl ether, 200 parts of

butanol and 620 parts of methanol is cast onto PETP film using a 0.25 mm doctor blade and dried at room temperature.

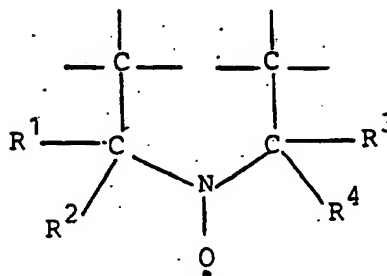
Subsequently the material is exposed for 30
5 seconds using an HBO 500 at a distance of 80 cm. After development with water a relief image is obtained which can be coloured, for example, with Solamin light Turkish blue.

If the unexposed material is stored for 2.5 hours
10 at 50°C and then exposed under the above-mentioned conditions, a strongly fogged relief image is obtained after development with water which, after colouring, has inadequate differences in colour density between the exposed and unexposed image areas.

Claims

1. A light-sensitive composition comprising a material that contains N-oxyl structural units having the formula I

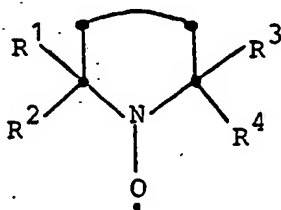
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in which R¹ to R⁴ may be the same or different and each represents H or alkyl.

2. A light-sensitive composition as claimed in claim 1, wherein the N-oxyl structural units are free and/or are in the form of polymer chain segments or substituents of a polymer that are fixed by means of Coulombic interactions and/or fixed by covalent bonding to the rest of the polymer.

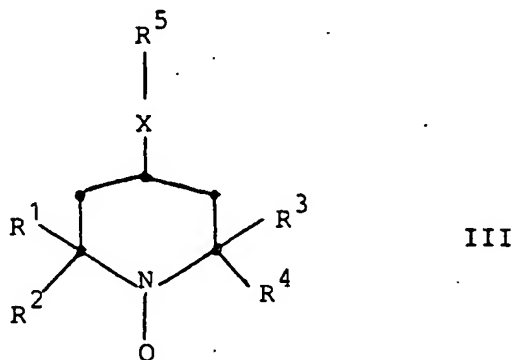
3. A light-sensitive composition as claimed in claim 1 or claim 2, wherein the N-oxyl structural unit is a sterically hindered cyclic 5- or 6-ring N-oxyl of the Formula II



II

in which R^1 to R^4 may be the same or different and each represents C_1 to C_4 alkyl.

4. A light-sensitive composition as claimed in claim 3, wherein the light-sensitive layer comprises a N-oxyl unit that is a 6-membered cyclic N-oxyl of the Formula III



in which

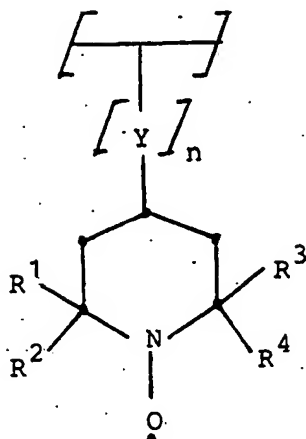
- R^1 - R^4 may be the same or different and each represents C_1 - C_4 alkyl,
 R^5 represents H, alkyl, aryl, acyl or a C_1 - C_{18} acid radical,

X represents $-NR^6-$, $-O-$, $-S-$ or $-C(=O)-$,
 R^6 represents H or CH_3

- and is present in the layer free and/or fixed by way of Coulombic interactions.

5. A light-sensitive composition as claimed in claim 3, wherein the light-sensitive layer comprises a polymer that contains a N-oxyl unit that is a 6-

membered cyclic N-oxyl of the Formula IV



IV

in which

R^1 - R^4 may be the same or different and each
represents C_1 - C_1 alkyl,

X represents $-NR^6-$, $-O-$, $-S-$ or $-C(=O)-$,

Y represents $-C(=O)-$, alkylene or $-NR^6-$,

R^6 represents H or CH_3

n represents 0 or 1,

and constitutes from 1 to 50 mole % of a copolymer.

6. A light-sensitive composition as claimed in claim 5, wherein the copolymer is a copolymer derived from polymerisation of two, three or more monomeric components.

7. A polymerisable material comprising a support and a light-sensitive layer comprising a light-sensitive composition as claimed in any one of claims 1 to 6.

8. A photopolymerisable material as claimed in claim 7, wherein the light-sensitive layer comprises at least one additional component selected from polymerisable monomers, initiators, binders and inhibitors.
- 5 9. A photopolymerisable material as claimed in claim 7 or claim 8, wherein the material comprises one or more additional auxiliary layers.
- 10 10. A photopolymerisable material as claimed in any one of claims 7 to 9, wherein the light-sensitive layer comprises a monomer and the concentration of the N-oxyl structural units is from 10 to 10^4 ppm based on the monomer.
- 15 11. A photopolymerisable material as claimed in any one of claims 7 to 10, substantially as described in any one of Examples 1 to 18 herein.
- 20 12. A method for the manufacture of a polymerisable material as claimed in any one of claims 7 to 11, wherein the light-sensitive layer is prepared by applying a solution or dispersion comprising the N-oxyl structural units to the support.
13. An image-bearing material that has been obtained by the image-wise exposure of a photopolymerisable

material as claimed in any one of claims 7 to 11,
followed by development.

14. A printed circuit or a printing plate that has
been manufactured by image-wise exposure to actinic
5 radiation of a polymerisable material as claimed in any
one of claims 7 to 11 and subsequent development.

15. Any novel feature herein disclosed or any
combination of herein disclosed features.